

125
17p
N 64 13283 *

CODE-1

(NASA CR-53012;
JPL-TR-32-518)

Technical Report No. 32-518

OTS: \$1.60 ph, \$0.80 mf

Some Experimental and Theoretical Significances
Associated With Irradiated Propellant

Anthony San Miguel and
Edward N. Duran

OTS PRICE

XEROX \$ 1.60 ph.
MICROFILM \$ 0.80 mf.



JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

November 1, 1963

17 p

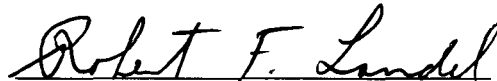
ref

Technical Report No. 32-518

*Some Experimental and Theoretical Significances
Associated With Irradiated Propellant*

Anthony San Miguel

Edward N. Duran

A handwritten signature in cursive script, reading "Robert F. Landel", written over a horizontal line.

Robert F. Landel, Chief
Polymer Research Section

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

November 1, 1963

Copyright © 1963
Jet Propulsion Laboratory
California Institute of Technology

Prepared Under Contract No. NAS 7-100
National Aeronautics & Space Administration

CONTENTS

I. Introduction	1
II. Theoretical Considerations	3
III. Experimentation	6
A. Swelling Test	6
B. Torsion Test	6
C. Uniaxial Tension Test	6
D. Multiaxial Tension and Compression Test	6
IV. Discussion	7
V. Conclusions	10
Nomenclature	10
References	11

TABLE

1. Comparison of torsion and tension test data	9
---	----------

FIGURES

1. Assumed cross-linked propellant-binder structure	2
2. Swelling phenomenon of propellant in benzene	3
3. Isotropic dewetting of propellant	4
4. Sol fraction as a function of irradiation	7
5. M_c as a function of irradiation	7
6. Stress vs. strain at different irradiation levels (uniaxial tension)	8
7. Ten-second modulus vs. temperature at different irradiation levels (torsion apparatus)	8
8. Uniaxial strain energy vs. first strain invariant	8
9. Multiaxial strain energy vs. first strain invariant	8
10. Strain energy ratio vs. irradiation for the four different experiments	9

ABSTRACT

13283

The mechanical properties of polyurethane solid propellant are degraded significantly by irradiation dosages greater than 10^6 rads. Four mechanical tests that provide sufficient data to characterize the degradation are described. These tests consist of (1) swelling, (2) torsion, (3) uniaxial tension, and (4) multiaxial tension and compression. The experimental data are characterized in terms of average molecular weight between cross-links (M_c), percent sol, small-strain shear modulus, tension modulus, and strain energy for increasing irradiation dosage. Comparisons between the various test data provide insight into the underlying effects of mechanical property degradation. Conclusions obtained in this study indicate that (1) the usefulness of M_c is questionable with regard to defining ionizing radiation degradation in a composite propellant such as polyurethane, (2) the torsion test is a simple and expedient method that may be used to study irradiated propellant quantitatively, (3) certain aspects of the kinetic theory of rubber elasticity are not quantitatively applicable to polyurethane propellant, and (4) the degradation response of irradiated propellant obtained from a uniaxial tension test typifies the degradation response of irradiated propellant obtained from multiaxial tests. R J T H O R

I. INTRODUCTION

Space missions are inherently subjected to a radiation environment (Ref. 1),¹ e.g., accumulative long-term storage in space. Consequently, the effects of irradiation upon the mechanical properties of solid propellant should be characterized. In this Report we attempt to describe the mechanical behavior of an ammonium perchlorate

polyurethane propellant at various stages of degradation due to gamma irradiation.

The mechanical properties, in the structural sense, are defined as the functional relationship between stresses and strains. Strain energy (Ref. 2) is one such function that is applicable to describe the elastic response (analogous to that of a mechanical spring) of a homogeneous, isotropic material. The presumption of any such function

¹Numbers in parentheses indicate References at the end of the Report.

is that an experimental method exists that is capable of measuring both the triaxial strains and stresses within a point region for some environment. From the molecular point of view, stress may be considered as the resultant of the Brownian motion of the molecules, as well as of the physical interactions between the molecules themselves, i.e., the sliding of molecules over each other. On a simple macroscopic scale, stresses for a composite propellant are distributed in some complex manner within the elastomer binder, the filler, and some boundary layer between the filler and elastomer. More specifically, a cross-linked polymeric binder, a crystalline oxidizer, and a metallic powder are all interacting in some manner.

For study on a microanalytical level, it is convenient to assume that the binder is made up of a triol cross-linked network (Ref. 3) such as the one illustrated in Fig. 1. Note that the oxidizer crystals are relatively so large that they would appear as a plane surface in this figure.

For such a model network it is convenient to visualize stress distributions in a manner similar to that used in frame structural analysis. It is evident that if structural members (molecules) are removed or severed from the network at random, then the remaining members will strain further to compensate for the increased member loads. The over-all structural strain energy required for the same deformation would be expected to decrease with removal of structural members. One effective

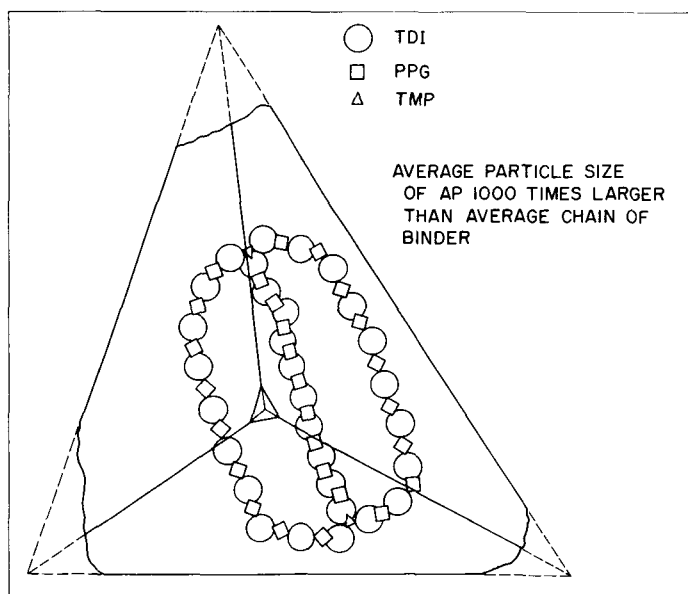


Fig. 1. Assumed cross-linked propellant-binder structure

method for removing structural members from the building network (binder) is to expose polyurethane to ionizing radiation.

Radiation damage in polymers results from the formation of foreign compounds in the material (Ref. 4). As energy packets traverse a material, they transfer energy to the electrons and nuclei of individual atoms in quantities sufficient to break the bonds or linkages which bind the atoms into molecular groups. Following the passage of the radiation particle, the fragments of the disrupted molecules react chemically to form compounds which differ from those originally present. The concentration of these impurity compounds increases with an increasing amount of radiation and results in a correspondingly greater change in the material's properties (Ref. 5). Chain scission occurs when there is a rupture of the primary valence link in the backbone chain of the polymer molecule.

It has been repeatedly confirmed that the major reactions in polymers, whether produced by fast electrons, X-rays or gamma rays, or mixed radiation including neutrons from atomic reactors, depend primarily on the total energy absorbed and sometimes on the radiation intensity, but rarely if ever on the type of radiation or its source (Ref. 6). Thus the irradiation damage discussed in this Report should be descriptive of damage due to radiation fields in general. The radiation dose unit used in this Report (rad) is defined as the absorption of 100 ergs of energy from the radiation particles per gram of material. The rad specifies only an amount of absorbed energy irrespective of the material, and hence cannot be used to describe a radiation field (Ref. 5).

It has been stated (Ref. 7) that radiation increases the sensitivity of explosives but that preignition or detonation will not occur. Only in rare cases has nuclear radiation been known to initiate explosives. Some explosives decrease only slightly in explosive efficiency and/or sensitivity, whereas others fail to perform their functions as primers or detonators. Propellants can be expected to follow the general trend of explosives.

Response of a polymer to irradiation (Ref. 8) may be described in two ways: (a) cross-linking of the polymer chains increases cross-link density, i.e., increases the number of network chains, and (b) scission of the molecular chains decreases the number of network chains, resulting in an increase in the average molecular weight between cross-links, M_c . Both processes occur simultaneously in many polymers, and the classification depends upon

which is predominant. Polyurethane rubbers are, as a class, among the most resistant rubbers (Ref. 9).

The oxidizer (ammonium perchlorate) and the aluminum filler degrade to a lesser degree than does the binder (Ref. 10). In any event the mechanical strength, except in compression, of a composite propellant is primarily a

function of the binder. In compression the extreme possibility would be that of a foam response of the propellant. However, it is believed that before any such mechanical degradation could occur, the ballistic characteristics of the propellant would have significantly deteriorated. Current state-of-the-art studies with irradiated propellant may be found in Ref. 10 to 14.

II. THEORETICAL CONSIDERATIONS

The characterization of irradiation damage should inherently be based on molecular phenomena. A possible theoretical basis may be founded on the kinetic theory of rubber-like materials (Ref. 15). This theory assumes that the elastic properties of a cross-linked binder are a function of the entropy decrease caused by boundary restraints via a statistically probable array of the cross-links. One basic assumption in this theory requires that the stress-temperature relationship of a medium should be primarily a function of entropy (to neglect the change in elasticity due to the internal energy contribution). It can be shown that a necessary result of this assumption is that the equilibrium stress (stress after essentially complete relaxation) must vary in direct proportion to the temperature. It is noted that this condition has not been verified for polyurethane propellants (Ref. 16, 17); i.e., they do not appear to exhibit this peculiar stress-temperature phenomenon. On the other hand, one would expect the unfilled binder to exhibit the direct stress-temperature relationship (Ref. 18). The theory also lends itself to elements of structural theory, such as strain energy and modulus. Thus, there would be merit in establishing the usefulness of the kinetic theory with regard to composite solid propellants.

A popular experiment associated with the kinetic theory of rubber-like elasticity consists of observing swelling phenomena (Fig. 2). The degree of cross-linking (Ref. 19, 20) relating to swelling may be approximated by

$$M_c = \frac{\rho V_1 \left[(v_2 v_0^2)^{1/3} - \frac{2v_2}{f} \right]}{-[\ln(1 - v_2) + v_2 + \chi_1 v_2^2]} \quad (1)$$

Various corrections should be applied to Eq. (1) to account for the filler content (Ref. 21 to 23). The object

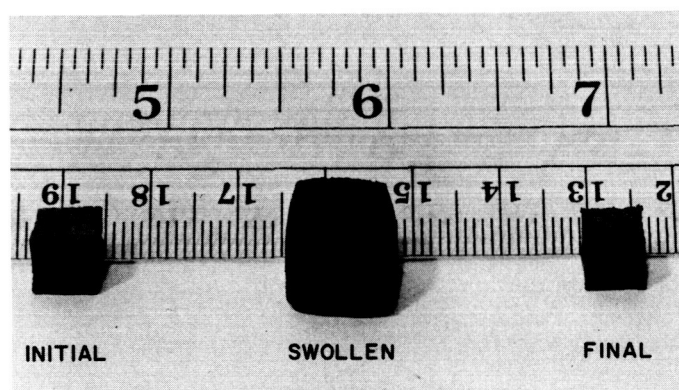


Fig. 2. Swelling phenomenon of propellant in benzene

is to obtain information regarding the number of cross-links in the binder network, hence a direct measurement of irradiation damage in the binder. The most influential correction to Eq. (1) is concerned with the filler-solvent correction factor. This accounts for the separation of the filler from the binder and the imbibition of "excess" swelling solvent. Figure 3 illustrates the complete dewetting of the oxidizer-binder surface and the associated swelling fluid (benzene) voids.

Equations (2) and (3) are the corrected values of v_2 and v_0 that may be used (Ref. 24) in conjunction with Eq. (1). These equations correct for the fluid voids and are valid only if there is an isotropic oxidizer-binder separation.

$$v_2 = \frac{V_F - V_E}{V_F + V_{ST} - V_E} \quad (2)$$

$$v_0 = 1 - \frac{V_E}{v_b V_F} \quad (3)$$

An analogous set of equations (2a and 3a) is here proposed to estimate v_2 and v_0 . These equations allow computations to be made when only the weights and densities

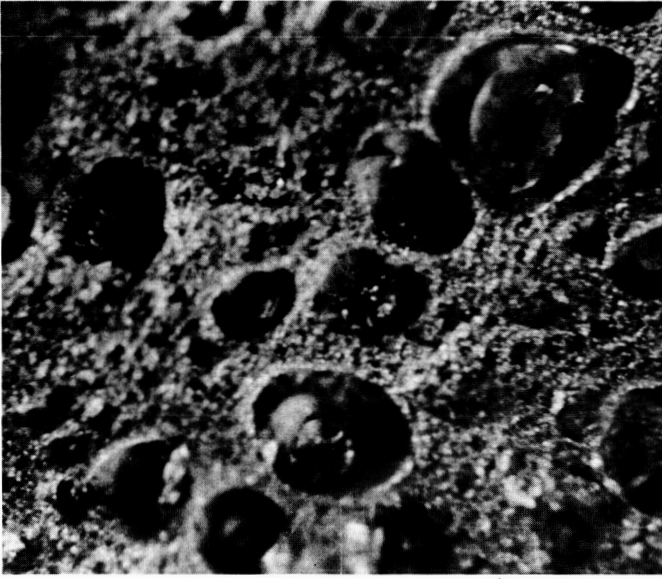


Fig. 3. Isotropic dewetting of propellant

are known for the binder (bi), propellant (pro), oxidizer (ox), and solvent. The validity of Eq. (2a) and (3a) has not been established.

$$v_2 \approx \frac{\frac{W_f}{\rho_{pro}} \left[\frac{\frac{wt\% bi}{\rho_{bi}}}{\frac{wt\% bi}{\rho_{bi}} + \frac{wt\% ox}{\rho_{ox}}} \right]}{\frac{W_f}{\rho_{pro}} \left[\frac{\frac{wt\% bi}{\rho_{bi}}}{\frac{wt\% bi}{\rho_{bi}} + \frac{wt\% ox}{\rho_{ox}}} \right] + \frac{W_s - W_f}{\rho_{solvent}}} \quad (2a)$$

$$v_0 \approx 1 - \left[\frac{\frac{W_i - W_f}{\rho_{bi}}}{W_i \frac{wt\% bi}{\rho_{bi}}} \right] \quad (3a)$$

The apparent molecular weight M_c obtained from Eq. (1) may be used via the kinetic theory to obtain the binder tensile modulus E_0

$$M_c = \frac{4pRT}{E_0} \quad (4)$$

Therefore, it is observed that the modulus-degradation relationship may be obtained from a swelling experiment utilizing the kinetic theory. The modulus thus obtained could presumably be compared with that obtained in any other fashion (a tension test) and thus establish the credibility of the procedure.

A problem arises in relating the modulus of the unfilled binder to that of the filled binder. The addition of filler increases the modulus in some unknown fashion. Various relationships have been proposed (Ref. 23, 25, 26); however, there currently appears to be a controversy as to what the functional relationship between the moduli should be. In any event, an approximate relationship appears to be described by

$$E = E_0 \left[1 + \frac{1.25 \phi}{1 - \frac{\phi}{\phi_m}} \right]^2 \quad (5)$$

It appears that $E \approx 20E_0$ for the polyurethane propellant in this study.

A swollen cross-linked polymer consists of two phases. The first phase, called the sol fraction s , is made up of the molecules which were linked together to form branched molecules of finite size. The second phase, called the gel fraction, consists of the molecules which have been linked together to form a three-dimensional network polymer of unlimited size.

The sol fraction characterizes the result of the radiation upon cross-links because it increases when degradation or chain scission occurs. This sol fraction s is calculated by

$$s = \frac{1}{v_b} \frac{W_i - W_f}{W_i} \quad (6)$$

A torsion apparatus may be used to measure an approximate initial shear modulus G . Such an apparatus may be constructed to the specifications of ASTM standards (Ref. 27); the basic theory is formulated in Ref. 28. The shear modulus obtained from such an apparatus can be calculated from

$$G = \frac{K(180 - \psi)L}{cd^3u\psi} \quad (7)$$

If an infinitesimal Poisson's ratio of the order of 0.5 is accepted as a fair approximation for propellant, then an initial modulus E can be computed from elasticity theory since

$$E \approx 3G \quad (8)$$

The uniaxial tension experiment is widely used because of its simplicity. The test consists of subjecting a JANAF specimen to uniaxial stress, τ_{11} . The longitudinal strain ϵ_{11} and lateral strains $\epsilon_{22} = \epsilon_{33}$ are measured in some manner, e.g., by measuring point displacements with a 70-mm camera. It is very difficult to measure an initial modulus with this test because of the uncertainty in the strain measurement for small strains.

It should be recognized that different investigators may read different significance into the uniaxial stress-strain curve. Disagreements arise concerning the effects on physical properties because of stress and strain rates, dewetting, reversibility, compression, triaxial extrapolation, creep, relaxation, healing, breaking, maximum stress, or strains and shifts. In any event, the uniaxial stress-strain curve is recognized as a permanent fixture in any mechanical property study. In this paper the immediate interest in the stress-strain curve is confined to the area under the curve and to the initial modulus. The significance of the area under the stress-strain curve will be based on the following considerations:

1. Reversibility of the stress-strain relationship can be obtained experimentally within 10% for at least two cycles up to 18% strain.
2. Creep is negligible during the cycling.
3. Relaxation is negligible during the cycling.
4. Dewetting is negligible to 10% strain (short time) and does not contribute to more than 20% "unloading" at 18% strain (short time). The over-all dewetting does not contribute more than 10% error to the "true" area under the stress-strain curve during the cycling.
5. Healing occurs at a similar rate as dewetting during the unloading portion of the cycle.

Uniaxial strain energy W_u is defined here as

$$W_u = \int_0^{\epsilon_{11}} \tau_{11} d\epsilon_{11} \quad (9)$$

For any given stress-strain curve, the area under the curve can be an approximate value for W_u . Noting the above restrictions, a 10% correction factor can be added.

The second problem that arises is a definition of modulus. In the classical sense, modulus is stress divided by strain. For a nonlinear material such as polyurethane propellant, its value changes from point to point. One useful modulus is the tangent modulus E_t , which is defined by the tangent to the stress-strain curve. The tangent modulus is defined as

$$E_t = \frac{d\sigma}{d\epsilon} \quad (10)$$

In the region of small strains the tangent modulus approaches the initial linear modulus. If the theory of

elasticity is assumed to be valid for infinitesimal strains, then the initial tangent modulus obtained from the tension test should compare favorably with the modulus obtained from the torsion test.

A method to measure a triaxial strain energy W_T is described in Ref. 2. The method consists of an inflated cylinder test in which the triaxial strains are measured and the triaxial stresses are computed. A possible expression for the strain energy function then becomes

$$W_T = \frac{\partial W}{\partial I_1}(I_1 - 3) + \frac{\partial W}{\partial I_2}(I_2 - 3) + \frac{\partial W}{\partial I_3}(I_3 - 1) \quad (11)$$

The interrelationship between modulus and strain energy for an elastic material that satisfies infinitesimal elastic theory is ($\mu = \frac{1}{2}$)

$$W_u = \frac{E\epsilon^2}{2} = \frac{\sigma^2}{2E} = \frac{3G\epsilon^2}{2} = \frac{\sigma^2}{6G} \quad (12)$$

according to the kinetic theory of rubber-like elasticity, the torsional strain energy W_m is

$$W_m = \frac{1}{2}G(I_1 - 3) = \frac{1}{2}N_0kT(I_1 - 3) \quad (13)$$

It can be shown (Ref. 29) that the strain invariants associated with the torsion of a right circular cylinder of homogeneous, isotropic, incompressible material may be expressed as

$$I_1 = I_2 = 3 + \psi^2 r^2 \quad I_3 = 1 \quad (14)$$

One can then assume that an approximate value for torsional strain energy in a rectangular beam takes the form

$$W_m = G(I_1 - 3) = G(\psi^2 r^2) \quad (15)$$

An approximate change in torsional strain energy with irradiation can thus be estimated for small shears as

$$\frac{W}{W_0} \approx \frac{G}{G_0} \quad (16)$$

Equations (1) to (16) represent physical property parameters that may possibly be applicable to describe irradiation degradation in the polyurethane propellant. Note that it is assumed throughout that the oxidizer is unaffected by the irradiation and that all the degradation in physical properties is due to changes in the bulk phase

of the binder, i.e., possible interfacial changes are also excluded. However, the information obtained from the above parameters is probably sufficiently accurate to use

with contemporary propellant structural analysis methods. As such, these results can serve as the basis for more advanced studies.

III. EXPERIMENTATION

Eighteen propellant specimens, which were supplied by the Jet Propulsion Laboratory (JPL), were divided into six groups. Each group consisted of the following:

1. One tubular propellant grain 3 in. in diameter and 4 in. long ($b/a = 2$).
2. One JANAF tensile bar.
3. One specimen for obtaining auxiliary data.

The specimens were irradiated with gamma radiation from the 10,000-Curie cobalt-60 facility at Aerojet-General Corporation. It was assumed that the samples were homogeneously irradiated. Dosimetry was performed during irradiation, and the following dosages were measured for the six groups:

Group	Irradiation, rad $\times 10^5$
1	4.4
2	24.3
3	75.1
4	119.2
5	145.7
6	0

After irradiation, the specimens were subjected to the tests described below.

A. Swelling Test

Four 0.25-in.³ samples were cut from the auxiliary specimen of each group, and their initial weights (W_i) were recorded. These propellant cubes were then immersed in 200 times their volume of anhydrous reagent benzene. All samples were then removed and weighed (W_s) after reaching their equilibrium swelling state. The absorbed solvent was removed from the samples by

drying in a vacuum. The final weight (W_f) was then recorded. By using Eq. (1), (2), and (3), M_c was then calculated, and the sol fraction s was obtained via Eq. (6).

B. Torsion Test

Samples were cut from the auxiliary specimen of each group, and were machined to the dimensions of $0.25 \times 1.50 \times 0.05$ in. These samples were immersed in a temperature-controlled silicone bath while the torsion head (not the propellant sample) was twisted through 180 deg (Ref. 27). The loading was maintained for 10 sec and the resulting angle ψ was read. The average molecular weight between cross-links M_c was approximated via Eq. (4), (5), (7), and (8). The angle of twist of the propellant sample is infinitesimal if a wire with a small torsion constant is used to apply a twist.

C. Uniaxial Tension Test

The JANAF tensile bars were elongated in a tension machine. Strains were computed from grid displacements via a 70-mm camera. True stress was computed from the tensile load and the actual cross-sectional area.

D. Multiaxial Tension and Compression Test

The inflated cylinder test, which consists of pressurizing a greased rubber bag within the cavity of the unrestrained propellant grain, measures both the tensile circumferential strains and the compressive radial strains, which are analogous to the strain states in operational motors. This test was applied to the propellant grain specimen in each test group. Triaxial strains were measured with a birefringent coating in conjunction with a longitudinal extensometer, and the three-dimensional stresses were approximated from the property-independent stress equations.

IV. DISCUSSION

Figure 4 illustrates how the sol fraction, Eq. (6), increases with greater irradiation dosage as a power function. The plot on log-log graph paper is linear and is typical of the values measured for an unfilled irradiated binder. Thus, it may be inferred that the propellant was irradiated in a random manner. The similarity between the sol fractions at the highest levels of irradiation indicates that the propellant samples may have received identical dosages or that a plateau was reached. The value of the swelling ratio q exceeded 11.5, indicating that a proper solvent (benzene) was used (Ref. 30). Another interesting observation is that an increase in sol fraction was observed for a second swelling experiment performed on a propellant that had been stored for 8 months after the first experiment. This indicates that degradation in terms of chain scission in the binder increased during this period.

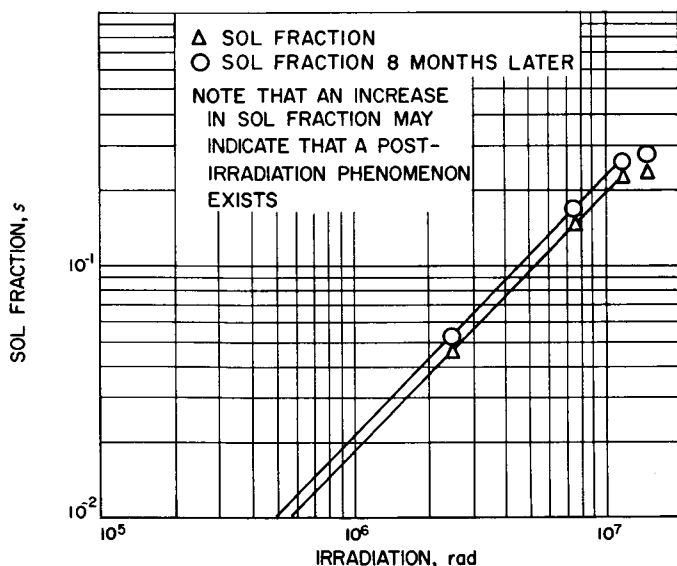


Fig. 4. Sol fraction as a function of irradiation

The molecular weight per cross-link (M_c) based on the kinetic theory of rubber-like materials (Eq. 1), increases with irradiation dosage as shown in Fig. 5. The value of M_c via torsional data, Eq. (4), is also shown in this figure. The disagreement is very evident. Factors that contribute to the discrepancy, aside from the basic theory, are dependent on the correction factor for filler material. Figure 3 illustrates the isotropic dewetting that occurs during swelling. Corrections for this phenomenon were questionable for the polyurethane propellant investigated

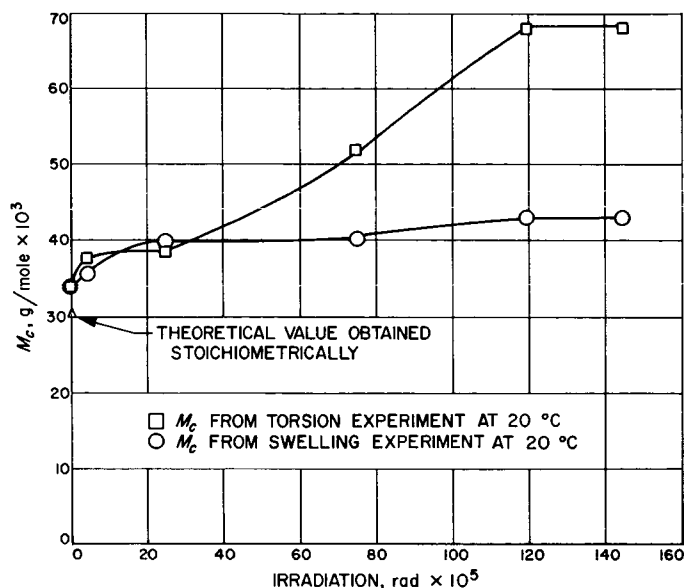


Fig. 5. M_c as a function of irradiation

(this may have been due to an excess of voids in the propellant). In any event, no significant volume change could be observed for the different irradiated samples whose initial dimensions were the same (Eq. 2 and 3). Thus Eq. (2a) and (3a) had to be used. The torsional data were also corrected for filler content (Eq. 5). Another observation not shown in the figure was that degradation due either to polyurethane-moisture degradation or to post-irradiation degradation was observed for swelling experiments performed upon the same propellant 8 months after the initial testing. The significance of this latter observation is that irradiation damage *may* increase with time even though the radiation field is removed. Further study of this observation is warranted.

The degradation of the tensile strength of the polyurethane is illustrated in Fig. 6 for the JANAF bars. The entire stress-strain curve is lowered for differing irradiation levels; thus the observation of maximum stress and strain as described in the literature should be sufficient to characterize irradiation damage.

The 10-sec shear modulus vs. temperature for various irradiation levels is shown in Fig. 7. This experiment was performed for infinitesimal strains. The modulus does not increase with temperature as would be required if the propellant followed the kinetic theory of rubber-like

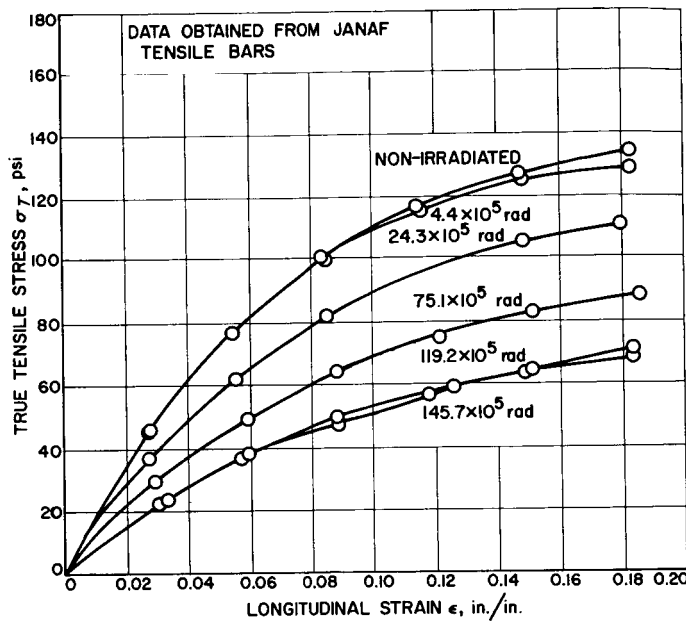


Fig. 6. Stress vs. strain at different irradiation levels (uniaxial tension)

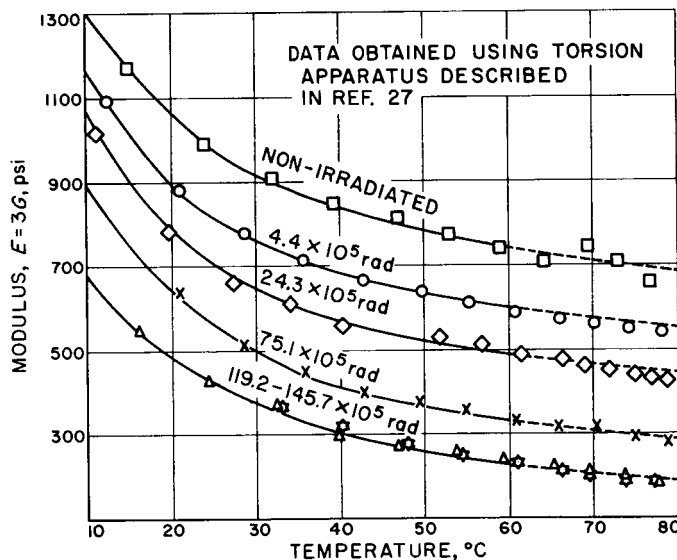


Fig. 7. Ten-second modulus vs. temperature at different irradiation levels (torsion apparatus)

elasticity. These data also agree with the tensile data found in Ref. 16 and 17.

A comparison between the initial modulus obtained for the shear experiment and the initial tangent modulus obtained graphically from Fig. 6 is shown in Table 1.

The comparisons are very favorable and suggest that the torsion experiment is a simple, expedient method to

measure changes in initial physical properties. For that matter, it is surmised that this simple torsion test may feasibly replace the tension test for quality control.

The uniaxial strain energy obtained from the tension data (Eq. 9) is shown in Fig. 8 as a function of the first strain invariant. The similarity to the stress-strain relationship is evident. The recoverable energy W_u decreases with irradiation, indicating degradation as would now be expected.

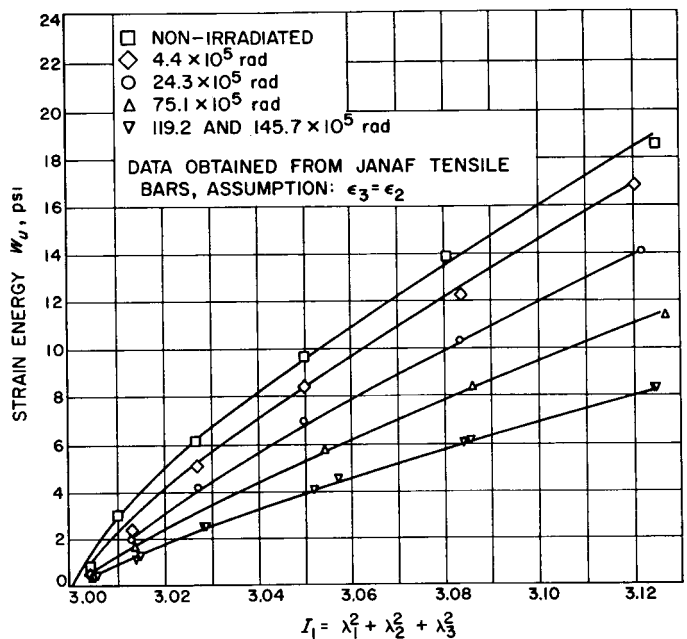


Fig. 8. Uniaxial strain energy vs. first strain invariant

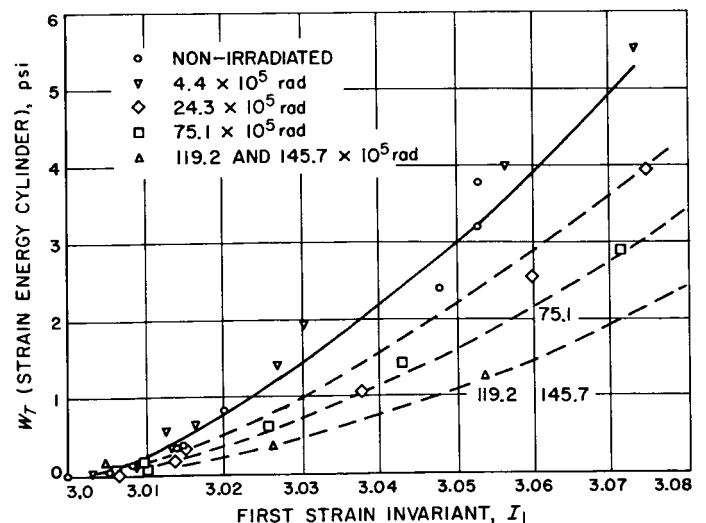


Fig. 9. Multiaxial strain energy vs. first strain invariant

Table 1. Comparison of torsion and tension test data

Irradiation dosage rad $\times 10^5$	Tangent modulus E_t (tension test), psi			Initial modulus E (torsion test), psi
	$\epsilon_1 = 0.02$	$\epsilon_1 = 0.04$	Average ϵ_1	
0	1,280	1,030	1,155	1,060
4.4	1,280	1,030	1,155	890
24.3	1,110	900	1,005	780
75.1	820	640	730	630
119.2	630	580	605	490
145.7	630	580	605	480

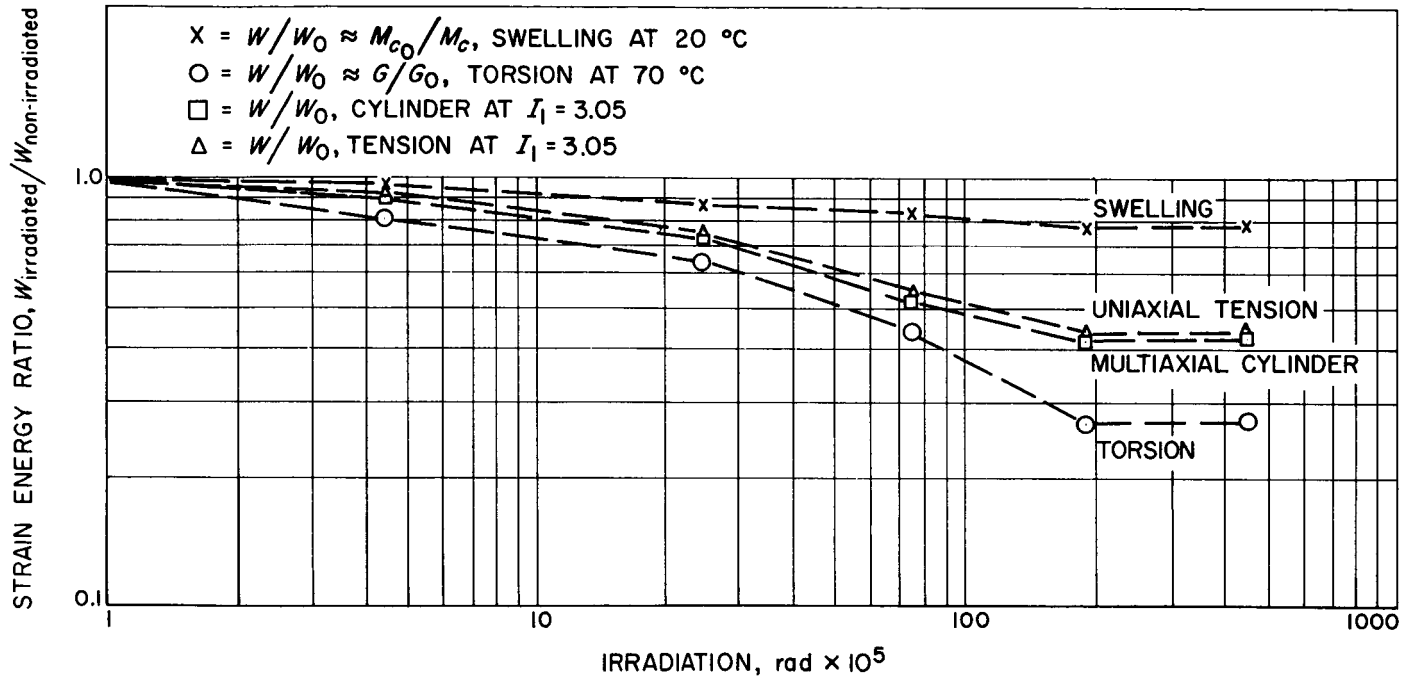


Fig. 10. Strain energy ratio vs. irradiation for the four different experiments

The multiaxial strain energy obtained from the inflated cylinder test (Eq. 11) is shown in Fig. 9 as a function of the first strain invariant. Comments similar to that for the uniaxial strain energy apply except that the magnitude of the multiaxial strain energy is about half that of the uniaxial strain energy.

A comparison between the ratio of the irradiated strain energy divided by the original strain energy for the vari-

ous experiments and the irradiation dosage is shown in Fig. 10. The uniaxial strain energy should be considered as the reference since it was obtained in the most direct fashion (Eq. 9). The multiaxial cylinder strain energy (Eq. 11) is seen to agree reasonably well with the reference. The torsional strain energy (Eq. 16) deviates considerably, although the basic degradation trend is evident. This deviation might have been expected since the strain energy ratio was only approximated; furthermore, the swelling strain energy ratio change is not reasonable.

V. CONCLUSIONS

The results obtained in this study indicate that:

1. M_c does not appear to be a sensitive measurement of degradation from ionizing radiation in composite propellant.
2. The torsion test is a simple and expedient method that may be used to study moduli quantitatively.
3. Certain aspects of the kinetic theory of rubber elasticity are not quantitatively applicable to polyurethane propellant.
4. The degradation response obtainable from a uniaxial test typifies the degradation response of irradiated propellant obtained from multiaxial tests.
5. The mechanical properties of polyurethane solid propellants degrade significantly for irradiation doses greater than 10^6 rads.
6. The sol fraction obtained with the swelling experiment is a useful indicator of degradation.

NOMENCLATURE

a	inner radius of a thick-wall cylinder, in.	q	$1/v_2$ = swelling ratio
b	outer radius of a thick-wall cylinder, in.	r	radius of a cylindrical specimen
c	width of torsion test specimen, cm	R	gas constant (1406.238 psi-cm ³ /mole-°K)
d	thickness of torsion test specimen, cm	s	sol fraction
E	tensile modulus of propellant, lb/in. ²	T	absolute temperature (°K)
E_0	tensile modulus of binder, lb/in. ²	u	a function of the cross-sectional geometry (Ref. 28)
E_t	tangent modulus	v_0	volume fraction of the relaxed network
f	functionality of the cross-linking, i.e., the number of chain ends united in one cross-link = 3 (Ref. 3, 30)	v_1	volume fraction of solvent
G	shear modulus, lb/in. ²	v_2	volume fraction of polymer in the swollen gel in equilibrium with the solvent
G_0	non-irradiated shear modulus	v_b	volume fraction of polymer in the original propellant
I_i	strain invariants	v_f	volume fraction
k	Boltzmann's constant	V	weight swelling ratio (the swollen weight W_s divided by the initial dry weight W_i) = $1/v_2$
K	torsion wire constant, g-cm/deg	V_1	molar volume of the solvent (89.4 cm ³ /mole, Ref. 3, Ref. 31)
L	length of torsion specimen, in.	V_E	volume of extractable polymer (sol)
M_c	average molecular weight between cross-links, gm/mole	V_F	original volume of propellant
n	number of moles of network chains per unit volume	V_{ST}	volume of solvent taken up by the specimen
n_1	mole fraction of solvent	W_f	final weight of propellant sample after sol extraction
N	number of lattice points in a crystal lattice	W_i	initial weight of propellant
N_0	number of network chains in a sample whose initial length and cross-sectional area are L and A , respectively		

W_m	torsional strain energy	ν	effective number of chains per unit volume
W_0	non-irradiated strain energy	ρ	density, g/cm ³
W_s	swollen weight of propellant and solvent at equilibrium	σ	stress, lb/in.
W_T	triaxial strain energy	ϕ	volume fraction of filler
W_u	uniaxial strain	ϕ_{\max}	maximum volume fraction of filler
ϵ_{ij}	strain, in./in.	χ_1	polymer-solvent interaction parameter (0.33, Ref. 32)
μ	Poisson's ratio	ψ	angle of twist of the torsion specimen, rad/in.

REFERENCES

1. Miller, R. A., and Cranford, W., *A Procedure for Calculating Radiation Exposure on Space Missions*, Nuclear Aerospace Research Facility, Report No. FZM-2655, General Dynamics, Fort Worth, Texas, August 16, 1962.
2. San Miguel, A., *An Experimental Method to Measure the Strain Energy Function W* , Technical Report No. 32-365, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, December 20, 1962.
3. Marsh, H. E., Jr., "Formulations and Quality Control in Polyurethane Propellants," *Industrial and Engineering Chemistry*, Vol. 52, September 1960, p. 768.
4. Harmon, Dale, J., *A Study of the Effects of Nuclear Radiation on Elastomeric Compounds and Compounding Materials*, WADC Technical Report 55-58, Pt. 5, B. F. Goodrich Co., Research Center, September 1959.
5. Collins, C. G., and Calkins, V. P., *Radiation Damage to Elastomers, Organic Liquids, and Plastics*, General Electric Co., Engineering TID 4500 (11th Ed.) APEX 261, published by Technical Publications GE-ANPD, Evendale, Ohio, September 1956.
6. Charlesby, A., *Effect of Radiation on Behavior and Properties of Polymers*, Chapter 10: "Effects of Radiation on Materials," J. J. Harwood, et al., ed., Rheinhold Publishing Corp., New York, 1958.
7. *Radiation Effects Methods and Data*, U.S. Air Force Nuclear Aircraft Research Facility, ANP. Document No. NARF 58-43T FZK-9-134, October 7, 1958.
8. Bovey, F. A., *Effects of Ionizing Radiation on Natural and Synthetic High Polymers*, Interscience Publishers, Inc., New York, 1958.
9. Wattier, J. B., et al., *Effects of Reactor Radiation on the Engineering Properties of Elastomers and Plastics*, Nuclear Aerospace Research Facility, Document No. NARF-62-5T FTZ-9-174, General Dynamics, Fort Worth, Texas, June, 1962.
10. Carleton, L. H., et al., *Effect of High and Low Intensity Radiation on Solid Composite Rocket Propellants*, Aerojet-General Corporation, Report No. 1764, Azusa, California, March 1960. CONFIDENTIAL

REFERENCES (Cont'd)

11. Hart, D. A., *A Review of the State of the Art on Solid Propellant Mechanical Properties in the United States*, Review Paper No. 5, Solid Propellant Information Agency, Johns Hopkins University, Baltimore, Maryland, July 1, 1962.
12. Fritz, E. G., and Johnson, P. M., *Tensile Behavior and Molecular Characteristics of Irradiated Elastomers*, USAF Nuclear Aerospace Research Facility, Document No. NARF-62-8T, MR-N-294, July 1962.
13. *Radiation Effects State of the Art 1961-62*, REIC Report No. 24, Radiation Effects Information Center, Battelle Memorial Institute, Columbus, Ohio, June 30, 1962.
14. Gardner, R. E., "Effects of Ionizing Radiation on Solid Rocket Motor Components," *ARS Journal*, Vol. 32, No. 7, 1962.
15. Treloar, L. R. G., *The Physics of Rubber Elasticity*, Oxford University Press, Amen House, London, 1958, p. 8.
16. Spangler, R. D., *Fracture Mechanics of Solid Propellants*, ELab-A-38, E. I. du Pont de Nemours and Co., Gibbstown, N. J., February 16 to September 30, 1961. CONFIDENTIAL
17. "Dynamic Mechanical Properties of Solid Propellant," *Quarterly Technical Summary Report*, January 1 to March 31, 1963, Atlantic Research Corporation, Alexandria, Virginia, May 10, 1963.
18. Fritz, E. G., and Johnson, P. M., "Stress-Strain Behavior of Irradiated Polyurethane Elastomers," *Journal of Applied Polymer Science*, Vol. 7, 1963, p. 1439.
19. Flory, P. J., and Rehner, J., Jr., "Statistical Mechanics of Cross-Linked Polymer Networks, II. Swelling," *Journal of Chemical Physics*, Vol. 11, 1943, p. 521; Flory, P. J., *ibid.*, "Statistical Mechanics of Swelling of Network Structures," Vol. 18, 1950, p. 108.
20. Hermans, J. J., "Deformation and Swelling of Polymer Networks Containing Comparatively Long Chains," *Transactions of the Faraday Society*, Vol. 43, p. 591, 1947; "Statistical Thermodynamics of Swollen Polymer Networks," *Journal of Polymer Science*, Vol. 59, 1962, p. 191.
21. Zapp, R. L., and Guth, E., "Elastic Modulus and Swelling of Butyl Vulcanizates," *Industrial and Engineering Chemistry*, Vol. 43, No. 2, February 1951, p. 430.
22. Kraus, G., "Swelling of Filler-Reinforced Vulcanizates," *Journal of Applied Polymer Science*, Vol. 7, 1963, p. 861.
23. Rutgers, R., "Relative Viscosity and Concentration," *Rheological Acta*, Vol. 2 (4), 1962, pp. 305-348.
24. Bills, K. W., Jr., and Salcedo, F. S., "The Swelling of Unfilled and Highly Filled Polymers," *Journal of Applied Physics*, Vol. 32, No. 11, 1961, p. 2364.
25. Landel, R. F., and Moser, B. G., "Relative Sedimentation Volume of Ammonium Perchlorate in Polypropylene Glycol," *Space Programs Summary No. 37-17*, Vol. IV, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 1962, p. 189.
26. Landel, R. F., and Smith, T. L., "Viscoelastic Properties of Rubberlike Composite Propellants and Filled Elastomers," *ARS Journal*, 31, May 1961, p. 599.

REFERENCES (Cont'd)

27. *Standard Method of Measuring Low Temperature Stiffening of Rubber and Rubber-like Materials by Means of a Torsional Wire Apparatus*, ASTM Document 1053-61, American Society for Testing and Materials, Philadelphia, 1961.
28. Timoshenko, S., and Goodier, J. N., *Theory of Elasticity*, McGraw-Hill Book Co., New York, 1951, pp. 272-278.
29. Green, A. E., and Zerna, W., *Theoretical Elasticity*, Oxford University Press, London, 1960, p. 84.
30. Flory, P. J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, p. 579.
31. Landel, R. F., and Fedors, R. F., "A Study of the Ultimate Properties of Amorphous Gum Vulcanizates," *Space Programs Summary No. 37-18*, Vol. IV, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 1963, p. 113.
32. Smith, T. L., and Magnusson, A. B., "Diisocyanate-Linked Polymers. II. Mechanical and Swelling Properties of Some Polyurethane Elastomers," *Journal of Polymer Science*, Vol. XLII, 1960, pp. 391-416.

ACKNOWLEDGMENT

The authors wish to acknowledge the advice and technical support of V. H. Culler, R. F. Fedors, R. E. Gardner, J. D. Ingham, and R. F. Landel.